



# Synthesis of ZSM-5 zeolite and silicalite from rice husk ash

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## ABSTRACT

Local rice husk was precleaned and properly heat treated to produce high purity amorphous  $\text{SiO}_2$  for use in the synthesis of ZSM-5 zeolite and silicalite by hydrothermal treatment ( $150^\circ\text{C}$ ) of the precursor gels (pH 11) under autogenous pressure in a short reaction time (4–24 h). A wide range of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratios (30–2075) and a small template content were employed to fully exploit the potential of rice husk ash (RHA). The mineralogical phases, morphology, specific surface area and pore volume of the synthesized products were investigated by XRD, FT-IR, SEM and BET analyses, respectively. Under the employed conditions, it was found that the gels with a low range of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratios ( $<80$ ) produced an amorphous phase to poorly crystalline ZSM-5 zeolite; those with a medium range (80–200) favored well crystalline ZSM-5 zeolite production with a large surface area; whilst those with a high range of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratios ( $>200$ ) yielded silicalite. The increase in  $\text{Na}_2\text{O}$  content, which was derived from the addition of  $\text{NaAlO}_2$  to attain the desired  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio of the gel, did not significantly enhance the crystallization rate, crystallinity, or yield of products. On the contrary, these properties were greatly affected by the increase in the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio.

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## 1. Introduction

Rice husk ash (RHA) is a solid waste product from the power generating industry which is suitable for recycling. The silica in rice husk is amorphous and transforms to crystalline silica when it is heated at high temperatures. The transformation temperature is affected by its chemical purity and particle size. In Thailand an enormous quantity of industrial waste grade RHA has been produced which directly affects upon the environment and imposes adequate storage problems and concerns. The International Agency for Research on Cancer (IARC) announced in 1997 that crystalline silica forms, such as quartz and cristobalite, belong to “Group 1” of hazardous materials which is the same group as asbestos. Accordingly, respirable crystalline silica is recognized as a material that can cause respiratory and other tissue damage including of cancer. To protect the environment and decrease the amount of RHA waste products requiring contained storage, finding an appropriate utilization of the ash is essential. It has been known that  $\text{SiO}_2$  in industrial waste RHA can exist in both amorphous and crystalline (mostly cristobalite) forms depending on its heat treatment history,

or, more precisely, the operating temperature characteristics of the boiler. The suspension type boilers produce mostly amorphous  $\text{SiO}_2$  whilst the Stoker types produce mostly cristobalite. Therefore, industrial waste RHA is a potentially attractive source for the large scale production of ZSM-5.

In addition to environmental and operative safety concerns, to be economically able to compete with established commercial ZSM-5 production, a simple and low cost production route has to be employed. Apart from the use of a low temperature hydrothermal reaction under autogenous pressure of the aqueous suspension, using a low cost but abundant and renewable source of  $\text{SiO}_2$  with high potential, i.e. fine grain, high porosity, large surface area, high purity and in an amorphous form, is promising since the crystallization time can be greatly reduced and a high yield attained. According to Mosungnoen and Wada [1], the amount of amorphous silica in Thai rice husk is about 20% (w/w). The ash from the unwashed husk contains about 96% (w/w) silica and some amount of organics, alkali oxide, and impurities but, with an appropriate washing of the husk, the ash can contain  $>99\%$  (w/w) silica. The alkalis, especially  $\text{K}_2\text{O}$  and  $\text{Na}_2\text{O}$ , in the rice husk accelerate the transformation of amorphous  $\text{SiO}_2$  to cristobalite or tridymite with a reduction in the transformation temperature from  $\sim 1200^\circ\text{C}$  in the absence of alkali to  $\sim 800^\circ\text{C}$  at low alkali contents ( $<1\%$ , w/w).

Although there have been many research documents encouraging the utilization of  $\text{SiO}_2$  from RHA for the synthesis

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**Table 1**  
Initial chemical compositions of the precursor gels.

SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O <sup>a</sup> /SiO <sub>2</sub>	NaAlO <sub>2</sub> (mg)	H <sub>2</sub> O (g)	NaOH (mg)	TPABr (g)	RHA (g)
30	0.212	209.8	49.2	424	0.5	2
50	0.194	124.7	49.2	424	0.5	2
80	0.182	76.8	49.2	424	0.5	2
100	0.177	60.8	49.2	424	0.5	2
200	0.169	28.9	49.2	424	0.5	2
400	0.165	13.1	49.2	424	0.5	2
800	0.163	4.9	49.2	424	0.5	2
1000	0.162	3.3	49.2	424	0.5	2
2075	0.160	–	49.2	424	0.5	2

<sup>a</sup> Total Na<sub>2</sub>O.

of various types of zeolite [2–4], the reported experimental results so far are equivocal in their potential suitability and optimal methods for utilization, due in part to the differences in the nature of the ‘as-prepared RHA’ and in the composition of the precursor gel. This hence leaves room for further refinements. As a part of a full-scale study on the viability of the synthesis method adopted by our research team, the following experimental results are presented: pretreatment of the rice husk and the effect of the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio on the crystallization rate, the crystallinity and stability of the zeolite. A locally obtained source of RHA was collected, washed first with water, and then with dilute HCl to reduce the alkali content, prior to burning of the ash. In the present study, we have performed a hydrothermal synthesis (150 °C) of a highly siliceous zeolite, of the type ZSM-5, under autogenous pressure, using a wide range of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratios, starting from 30 up to 2075, the latter limit of which is the original ratio of the RHA silica.

## 2. Experimental

### 2.1. Materials

RHA silica was prepared by burning the acid leached rice husk [5] at 700 °C for 3 h followed by sieving through a mesh number 230 screen (as-prepared RHA silica, BET surface area = 240 m<sup>2</sup>/g) and grinding to fine powder in a pulverizer. The obtained white ash, as agglomerates of ground RHA silica, with a SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio of 2075, consisted of amorphous SiO<sub>2</sub>. Sodium aluminate (NaAlO<sub>2</sub> powder, Riedel-de Haën), tetrapropylammonium bromide (TPABr powder, Merck), sodium hydroxide (NaOH pellets, Merck) and nitric acid (AnalaR) were used as source of alumina, template, alkali and pH regulator, respectively.

**Table 2**  
The chemical analysis (XRF) and BET surface area of RHA silica.

Chemical composition	wt%
SiO <sub>2</sub>	99.64
Al <sub>2</sub> O <sub>3</sub>	0.08
K <sub>2</sub> O	0.04
Na <sub>2</sub> O	0.00
P <sub>2</sub> O <sub>5</sub>	0.10
CaO	0.04
SO <sub>3</sub>	0.03
Fe <sub>2</sub> O <sub>3</sub>	0.04
CuO	0.01
MoO <sub>3</sub>	0.01
Others	0.03

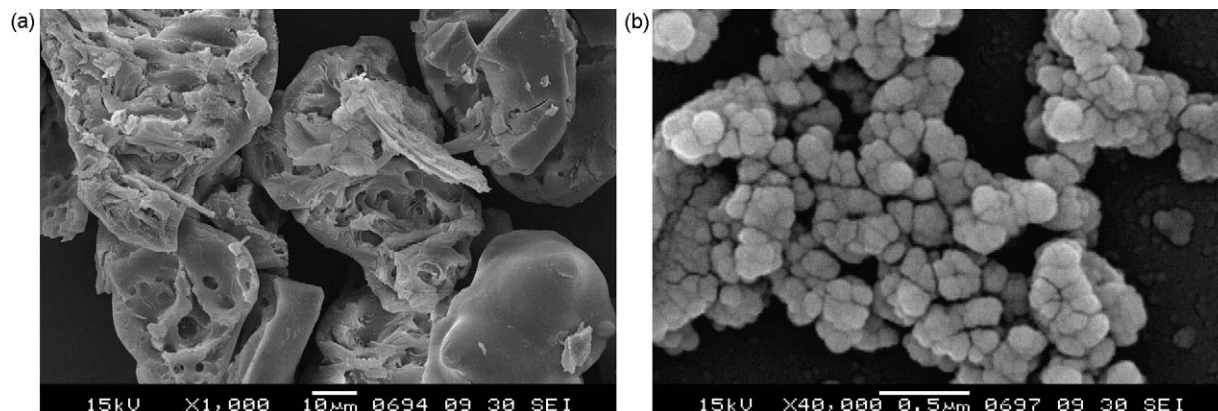
SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio = 2075. Average particle size (SEM) of the ground RHA silica ~0.1 μm.

### 2.2. Methods

The hydrothermal synthesis of ZSM-5 zeolite was performed in a stainless steel bomb lined with PTFE under autogenous pressure at different SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratios, from the as-prepared ground RHA silica, under hydrolysis at 150 °C for 48 h, using a low concentration of TPABr as the organic template. The preparation of the precursor gels was performed by a modification to that of Mohamed et al. [6]. Briefly, 2.0000 g finely ground RHA silica and 0.18 mol/L TPABr solution were mixed with 0.27 mol/L NaOH solution in a final volume of 50 mL and the resultant suspension was stirred for 30 min at room temperature. An aqueous solution of sodium aluminate was prepared separately by mixing a calculated proportion of sodium aluminate and 0.27 mol/L NaOH solution to obtain the gel with a desired SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio (Table 1). The sodium aluminate solution was then added to the suspension with stirring for 1 h at room temperature. The pH of the gel was adjusted to about 11 by the addition of 1 mol/L HNO<sub>3</sub> acid before hydrothermal treatment at 150 °C. After each time interval, the obtained product was separated by centrifugation, washed with distilled water, dried at 80 °C for 12 h and calcined in air at 550 °C for 5 h to remove the organic template, cooled in desiccators and then weighed to four decimal places. The weight obtained based on the weight of the ground RHA silica plus Al<sub>2</sub>O<sub>3</sub> (in the NaAlO<sub>2</sub> powder) was taken as the product yield (wt%) [7].

### 2.3. Characterization

The chemical analysis of the RHA silica was performed by X-ray fluorescence (XRF) with a Philips PW 1480 spectrometer. The



**Fig. 1.** Representative SEM micrographs of (a) as-prepared RHA silica grains and (b) agglomerates of ground RHA silica.

**Table 3**

The chemical composition and mineral phase of ZSM-5 zeolite and silicalite.

SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> molar ratio in the gel	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> molar ratio in the zeolite	Synthesis time (h)	Phase formed	Synthesis yield <sup>a</sup> (%)
30	n.d.	120	Amorphous, ZSM-5 <sup>b</sup>	n.d.
50	n.d.	72	Amorphous, ZSM-5 <sup>b</sup>	n.d.
80	120	24	ZSM-5 zeolite	84.1 ± 0.49
100	157	12	ZSM-5 zeolite	71.8 ± 0.74
200	163	12	ZSM-5 zeolite	70.2 ± 1.79
400	Only SiO <sub>2</sub>	6	Silicalite	60.1 ± 0.65
800	Only SiO <sub>2</sub>	6	Silicalite	57.8 ± 0.89
1000	Only SiO <sub>2</sub>	4	Silicalite	56.9 ± 1.00
2075	Only SiO <sub>2</sub>	4	Silicalite	56.8 ± 1.08

n.d. = not determined.

<sup>a</sup> Data for the % synthesis yield are the mean taken from 3 separated runs (95% confidence level).<sup>b</sup> Poorly crystalline ZSM-5 zeolite.

morphologies of the RHA and the obtained ZSM-5 zeolite and silicalite were observed by scanning electron microscopy (SEM) using a JEOL JSM 6400. The contents of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> in the zeolite were determined by the EDAX technique and X-ray diffraction (XRD) patterns were collected by Bruker, D8 Advance. The FT-IR spectra were recorded using a PerkinElmer (Spectrum One) spectrometer. The BET specific surface area and the BJH pore size distribution were measured using a Coulter SA 3100.

### 3. Results and discussion

#### 3.1. Characterization of the starting materials and the products

The chemical composition and physical properties of the RHA silica as-prepared are summarized in Table 2, and reveal a very high purity SiO<sub>2</sub>. Moreover, it is interesting that all the Na<sub>2</sub>O and much of the K<sub>2</sub>O have been washed out. However, due to the strong agglomeration of the ground RHA, its average particle size had to

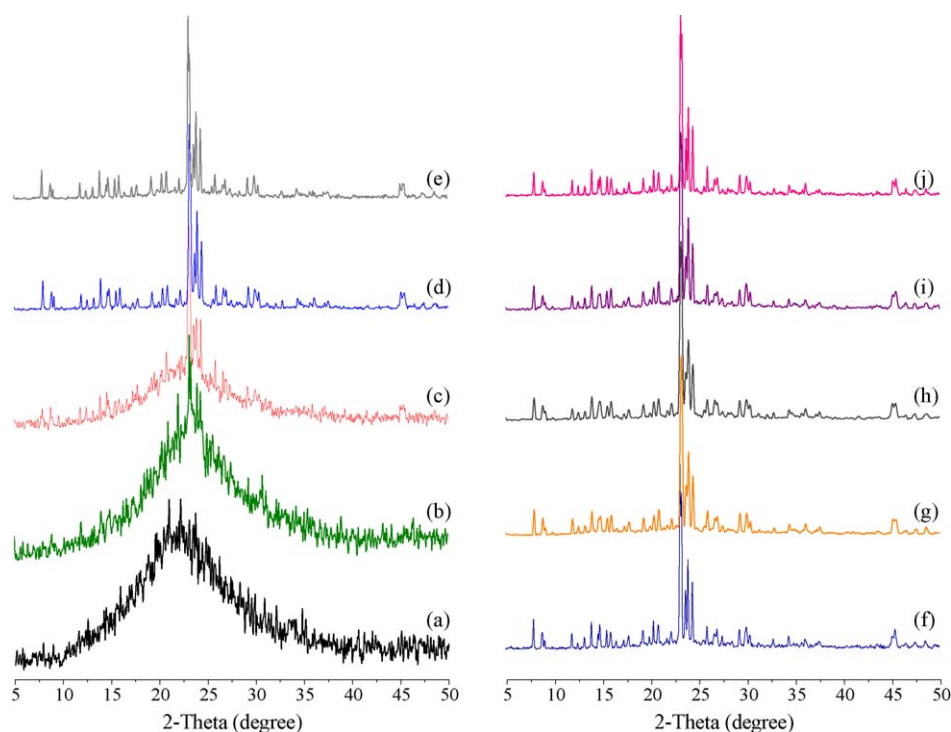
**Table 4**The effect of varying the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio on the BET surface area and the pore size of the obtained ZSM-5 zeolite and silicalite.

SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> molar ratio in the gel	BET surface area (m <sup>2</sup> /g)	Micropore volume (cm <sup>3</sup> /g)	Mesopore volume (cm <sup>3</sup> /g)	Total pore volume (cm <sup>3</sup> /g)
30	27	0.0059	0.0258	0.0358
50	82	0.0148	0.0254	0.0605
80	306	0.1050	0.0214	0.1454
100	308	0.1090	0.0306	0.1758
200	365	0.0962	0.0235	0.1871
400	215	0.0878	0.0343	0.1384
800	185	0.0660	0.0330	0.1264
1000	172	0.0390	0.0377	0.1264
2075	122	0.0166	0.0697	0.1241

be estimated from the SEM micrographs, an example of which is shown in Fig. 1.

From preliminary experiments, using a stainless steel bomb lined with PTFE under autogenous pressure at different SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratios, a well crystalline ZSM-5 was obtained at a SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio of 80 under hydrolysis at 150 °C for 48 h, using 0.9 mol/L TPABr as the organic template (data not shown). Moreover, when using ground RHA silica, ZSM-5 with high crystallinity could be obtained at the same temperature in only 24 h without increasing the template content (data not shown). Therefore, in this study ground RHA silica and a reduced template concentration were employed to reduce both the organic template content and the reaction time.

Table 3 shows the chemical compositions, mineral phases, synthesis times and the yield of the products obtained at the optimized synthesis times. The range of synthesis times investigated in each experiment was determined according to the range of the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio. That is for low SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratios, of 80 and less, they were assayed after 10, 12, 22, 24, 30 and 120 h; whilst for higher SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratios, of 100 and above, they were assayed after 2, 3, 4, 5, 6, 10 and 12 h. Since it is well



**Fig. 2.** Representative XRD patterns of as-synthesized samples obtained at different SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratios. XRD derived diffractograms obtained from: (a) RHA, and from SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratios of (b) 30, (c) 50, (d) 80, (e) 100, (f) 200, (g) 400, (h) 800, (i) 1000 and (j) 2075.

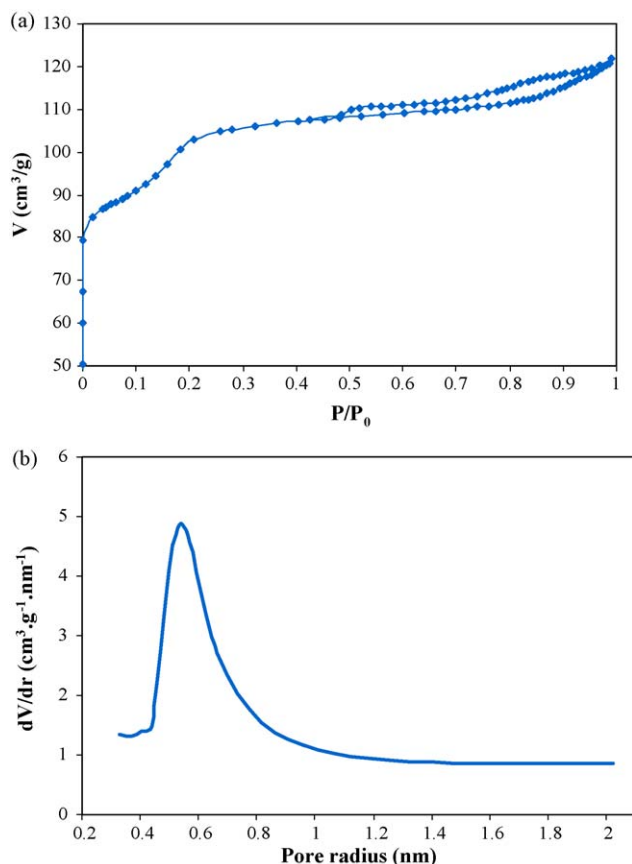


Fig. 3. (a) Nitrogen isotherm and (b) pore size distribution curve of ZSM-5 ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 200$ ).

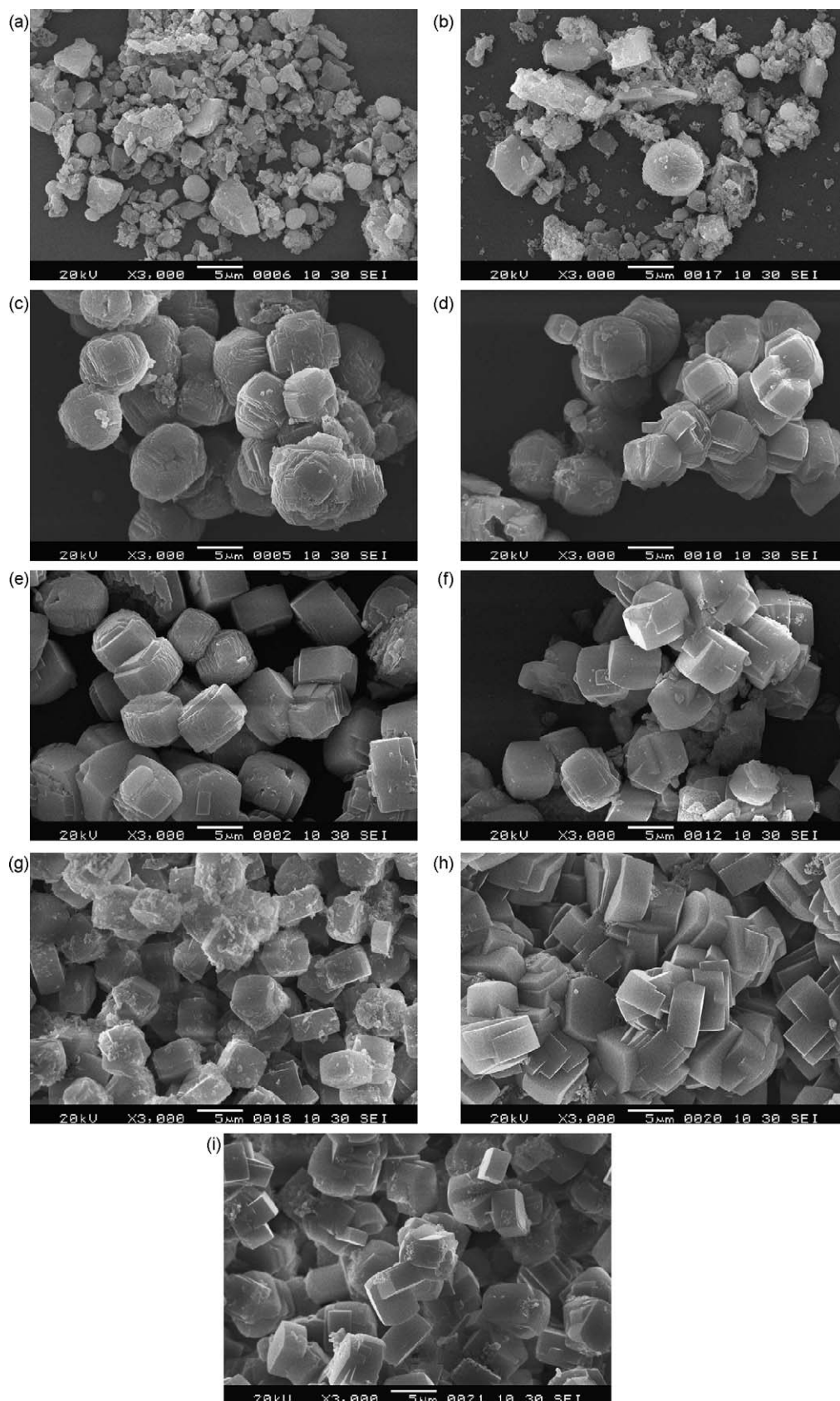
known that the surface area, crystallinity and mineral phase of the hydrolysis product varies along the course of hydrothermal treatment [8], the optimization is based on the conditions revealed by the XRD that first gave well crystalline ZSM-5 with no trace of the amorphous RHA silica (hump around  $22^\circ 2\theta$ ).

The XRD results (Fig. 2) clearly revealed that the crystallinity of ZSM-5 increases with increasing  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratios.  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratios from 80 to 2075 produced a single phase of well crystalline ZSM-5 in a short time (24–4 h), whilst  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratios below 80 (i.e. 50 and 30), yielded poorly crystalline ZSM-5 and an amorphous phase was principally formed instead. This finding agrees well with the report of Szostak [9] that the crystallization rate for the formation of ZSM-5 increased: (i) as the aluminum content decreased, (ii) with a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio above 100, and (iii) that the greater the NaOH concentration, the lower the yield of the crystalline material attained. Despite keeping the pH of each gel around 11 with the addition of  $\text{HNO}_3$  in our gel preparation, the total NaOH concentration of the gel varied depending on the content of  $\text{NaAlO}_2$  added in order to set the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio (Table 1). Hence gels with a high ratio of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  contain a low NaOH content, promoting the formation of a high  $\text{SiO}_2/\text{Al}_2\text{O}_3$  zeolite due to the low relative solubility of the  $\text{Al}^{3+}$  ion with respect to the  $\text{Si}^{4+}$  ion in alkaline NaOH solutions. However, in this experiment, it was found that the maximum yield of ZSM-5 zeolite at 84% (w/w) was obtained at a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 80, and that as the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio increased above 80 then so the yield of the product tended to decrease. The  $\text{Al}_2\text{O}_3$  content in the ZSM-5 attained from a high  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio ( $\geq 400$ ) might be too small to be detected by EDAX. According to Szostak [9], the pure silica polymorph of zeolite ZSM-5 was named 'silicalite or silicalite-1'.

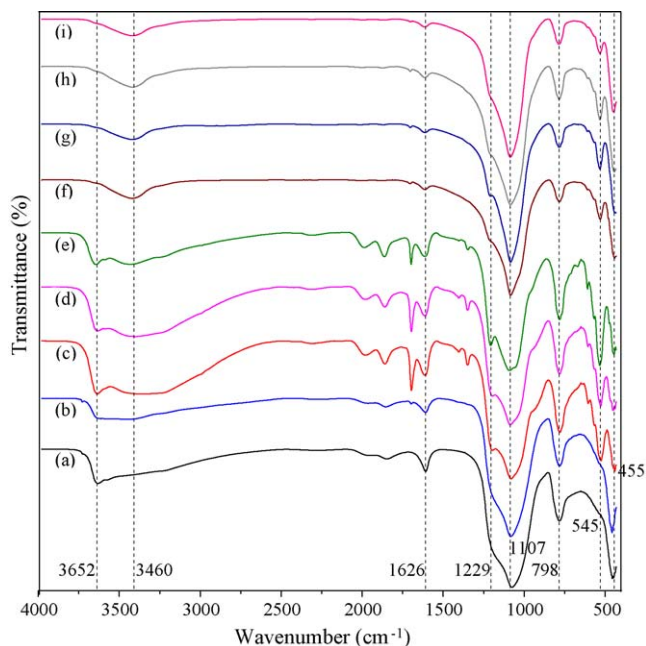
The results summarized in Table 4 show that with increasing  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratios, the surface area and the micropore volume of the product initially dramatically and dose-dependently increase and reach a maximum at a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio of 200. Further increases in this molar ratio beyond 200, however, leads to a dose-dependent gradual decrease. This presumably resulted from crystal linkage leading to the formation of thin plates of aggregates.  $\text{N}_2$  adsorption–desorption isotherms of calcined samples with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratios of 80–400 were measured at  $-196^\circ\text{C}$ . They all revealed microporosity as a sharp knee at  $P/P_0$  lower than 0.1 due to filling of micropores and capillary condensation as an adsorption hysteresis loop at higher  $P/P_0$  which is characteristic of Type IV isotherms. As a representative, the isotherm and the pore size distribution curve of ZSM-5 with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio of 200 are shown in Fig. 3(a) and (b), respectively. The median pore radius inferred from the curve is about 0.5 nm. The SEM micrographs of the hydrothermal products (Fig. 4) reveal the morphologies of the products at different  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratios. At low  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratios ( $<80$ ) principally fragmented amorphous material and spheres of poorly crystalline zeolite were obtained, whilst with higher  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratios ( $\geq 80$ ) well crystalline zeolite, with an average crystallite size of 6–7  $\mu\text{m}$ , was obtained. It was also clearly noticed that the crystalline ZSM-5 with a large surface area obtained from  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratios of 80–800 has a round shaped crystal and is less aggregated, whilst those obtained from the higher  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratios ( $>800$ ) are more tubular and strongly aggregated. The surface area of over  $300 \text{ m}^2/\text{g}$  is quite reasonable for the large sized and well-crystallized ZSM-5 ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 80$ –200) regarding to the previous reports [4,10,11].

Infrared spectroscopy was also used to follow the effect of different  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratios on the zeolitization process. Representative FT-IR spectra of the synthesized products after calcining, to get rid of the template, at  $550^\circ\text{C}$  are shown in Fig. 5. According to Kordatos et al. [4] the vibration modes near 1100, 800 and  $450 \text{ cm}^{-1}$  are assigned to the internal vibrations of Si and  $\text{AlO}_4$  tetrahedra in silica, quartz and cristobalite, respectively, whilst the vibration modes near 550 and  $1230 \text{ cm}^{-1}$  are assigned to the double-ring tetrahedral vibration and asymmetric stretching of Si and  $\text{AlO}_4$  tetrahedra in the zeolite framework, respectively. It is clearly seen that these vibration modes (internal and external) appear in all the synthesized samples but the characteristic vibration mode of the ZSM-5 framework at  $1230 \text{ cm}^{-1}$  is better resolved in the samples derived from  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratios ranging from 80 to 200. This coincides with the transition of ZSM-5 zeolite to silicalite at a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio of  $>200$  (Table 3). It is worth noting that according to Szostak [9], the crystallization of ZSM-5 structure occurs over a wide range of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratios (from 15 to  $\infty$ ) but that the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio of 190 is the maximum ratio for an aluminosilicate to be defined as 'zeolite'. Moreover, the sharpness and intensity of the absorption band near  $550 \text{ cm}^{-1}$  in the samples derived from a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio of more than 80 confirm the high degree of crystallinity of ZSM-5 that was also revealed by XRD and SEM analyses. The bands at around  $1600 \text{ cm}^{-1}$ , attributed to the bending of molecular adsorbed water, revealed in the samples derived from a low  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio were also more clearly resolved in samples derived from  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratios of 80 to 200. This indicates a high microporosity [12] which is in accordance with the results of surface area and micropore analyses presented in Table 4. In addition, the bands near  $3652$  and  $3400 \text{ cm}^{-1}$ , attributed to the stretching vibrations of the bulk silanol groups and molecular water  $\text{OH}^-$  groups and/or silanol group H ions, are present in samples derived from  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratios of 80 to 200, but only the band at around  $3400 \text{ cm}^{-1}$  persists throughout this range of samples. This





**Fig. 4.** Representative SEM micrographs of various as-synthesized ZSM-5 zeolites derived from  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratios of (a) 30, (b) 50, (c) 80, (d) 100, (e) 200, (f) 400, (g) 800, (h) 1000 and (i) 2075.



**Fig. 5.** Representative FT-IR spectra of calcined ZSM-5 derived from  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratios of (a) 30, (b) 50, (c) 80, (d) 100, (e) 200, (f) 400, (g) 800, (h) 1000 and (i) 2075.

indicates the reduction of Si–OH groups in the samples with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratios over 200.

#### 4. Conclusion

The fine grain size with a large surface area, high degree of purity and the amorphous state of RHA silica combined with the constrained composition ( $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio) of the precursor gel, which enhances the dissolution of silicate and aluminate species, serve to thermodynamically speed up the nucleation and crystallization rate, and stability of ZSM-5. As a result, well crystalline ZSM-5 zeolite with a large surface area and well crystalline silicalite are successfully synthesized from RHA silica by

hydrothermal hydrolysis at 150 °C under autogenous pressure in a short reaction time, 4–24 h. The maximum yield of zeolite, at 84% (w/w), was obtained at a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio of 80, and the transition of ZSM-5 zeolite to silicalite occurs at  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio of >200. This also demonstrates that without additional  $\text{Al}^{3+}$  ions, the original  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratios (2075) of the RHA silica alone can produce silicalite.

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